Photochemical Conversion of Colupulone into 4-Deoxycohumulone

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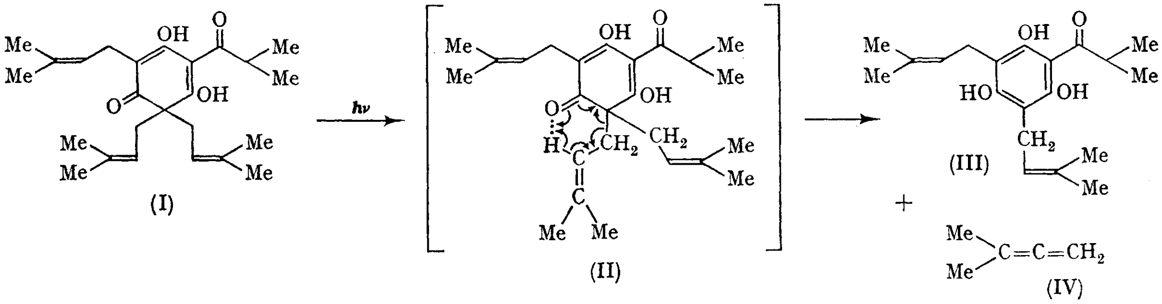
IRRADIATION of a 10^{-3} M solution of colupulone (I) in propan-2-ol or methanol in a Rayonet photochemical reactor (3500 Å) under nitrogen for seven days results in the formation of a 4-deoxycohumulone,[1] (III), as the primary product. The reaction was monitored by observing the disappearance of the u.v. maximum at 255 mμ and appearance of a band at 290 mμ.



Complete removal of solvent left a residue which on recrystallization from pentane yielded (65%) needles, m.p. 88—89° (lit.,[2] m.p. 88—89°), *M*, 332. Its u.v. spectrum showed absorption at λ_{max} (EtOH) 290 mμ (ϵ 18,280) and λ_{min} 235 mμ (ϵ 3280).[1] The i.r. spectrum (CCl_4) showed significant peaks at 3600 (free OH), 3400 (OH with intramolecular hydrogen bonding), 1665 (C=C), 1615 [C=O of the type $(HO)_2Ar\text{-}C{=}O$], 1595 and 1300—1450 (aromatic ring vibrations), 1380 (*gem*-di-Me), and 1230 cm.$^{-1}$ (C–O of an aromatic phenol). The n.m.r. spectrum (CCl, 60 MHz.) was in excellent agreement with compound (III). The resonance positions in p.p.m. to low field from Me_4Si were: δ 1·1 (6H, doublet), 1·7 (2H, doublet), 1·9 (12H, doublet), 2—3 low unresolved peaks), 3·3 (2H, doublet), 3·8 (1H, triplet, 5·2 (2H, triplet), and 9·99 (1H, broad singlet).

No photoreduction of colupulone appears to take place. It is known[2] that benzophenone and other substituted ketones can be easily photoreduced to pinacols in propan-2-ol and other alcoholic solutions. This finding represents an interesting photochemical reaction wherein there is no incorporation of alcohol solvent in colupulone.

Formation of (III) appears to take place through a photocycloelimination process (Norrish type II reaction) proceeding through the short-lived six-membered cyclic transition state (II). Moreover, a vast improvement of yield can be obtained by this photochemical technique (75%) as compared to 2·7%,[1] by the conventional chemical synthesis.

Further investigations on the reactions of light with colupulone and other bitter, non-volatile constituents of hops are in progress.

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[1] H. Hubner, J. Maier, and W. Riedl, *Z. physiol. Chem.*, 1961, 325, 224.

[2] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, 1965, p. 139.